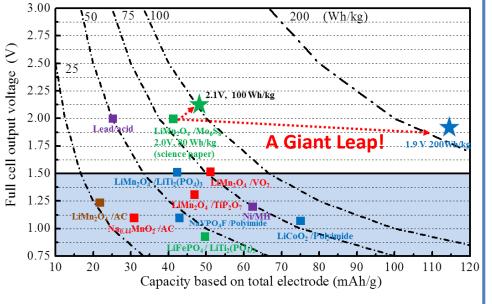
Multiple Electron Aqueous Li-ion Batteries

Technology Overview

- The electrochemical stability window of aqueous electrolyte has been expanded to ~3.1 volts via the formation of SEI.
- A 1.9 V full cell using such electrolyte delivers a record-high 200 Wh/kg (based on two electrode mass) for 200 cycles.



TEAM

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Current Status

- (1) STATUS: A safe 1.9V cell using 3.1V aqueous electrolyte can stably provide 200 Wh/kg (anode+cathode mass) for 200 cycles.
- (2) **NEXT TECHNICAL:** reducing cost of electrolytes
- (3) **NEXT COMMERCIAL**: Is collaborating with Saft American Inc. to build a 500 Wh demonstration unit.
- (4) HELP NEEDED: Cost modeling expert & new salts

Project Statistics

Award Amount	\$1.1M
Award Timeline	Dec. 2013 – May. 2016
Next Stage Target	500 Wh prototype unit
Partners Sought	Saft, ARL, US TARDEC



vs. Li/Li+

Expanded Electrochemical Stability Window:

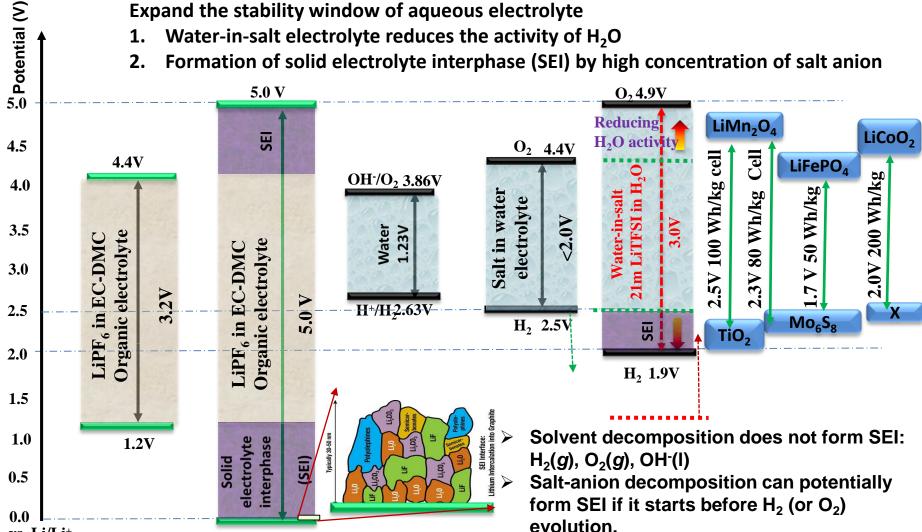
From 1.23 V to 3.0 V

Energy density $E = cell \ voltage \ V \times capacity \ Q$

Electrochemical stability window of Electrolyte control the cell voltage

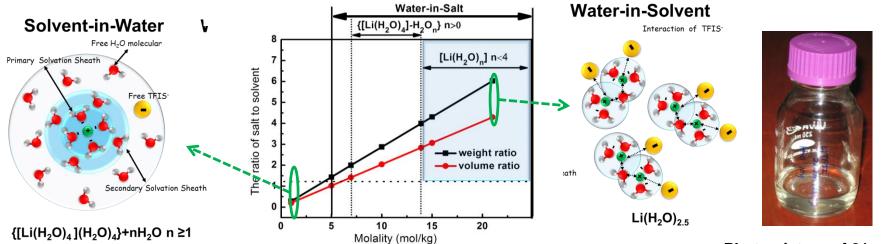
Expand the stability window of aqueous electrolyte

Water-in-salt electrolyte reduces the activity of H₂O



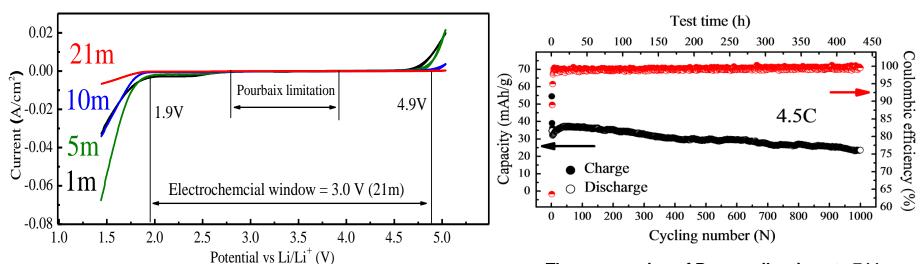


21 m Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in water electrolyte



The change of weight and volume ratio of LiTFSI to $\rm H_2O$ with the molarity of LiTFSI in $\rm H_2O$

Photo picture of 21 m LiTFSI aqueous electrolyte



The electrochemical stability window

The progression of Raman vibration at ~744 cm⁻¹ with salt concentration;

Achievement reported in paper at Science

- Formed SEI for the 1st time in aqueous electrolytes
- Expanded electrochemical stability of aqueous electrolytes to 3.0 V
- Assembled a 2.3 V aqueous LIB that cycled >1000 times at ~100% CE
- Energy density: 80~100 Wh/(Kg of total electrode mass);
- Stability at both low (0.15 C) and high (4.5 C)
- Absolutely safe

RESEARCH | RESEARCH ARTICLES

Corrected 24 November 2015; see full text.

BATTERIES

"Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries

Liumin Suo, ¹ Oleg Borodin, ² Tao Gao, ¹ Marco Olguin, ² Janet Ho, ² Xiulin Fan, ¹ Chao Luo, ¹ Chunsheng Wang, ^{1*} Kang Xu^{2*}

Lithium-ion batteries raise safety, environmental, and cost concerns, which mostly arise from their nonaqueous electrolytes. The use of aqueous alternatives is limited by their narrow electrochemical stability window (1.23 volts), which sets an intrinsic limit on the practical voltage and energy output. We report a highly concentrated aqueous electrolyte whose window was expanded to ~3.0 volts with the formation of an electrode-electrolyte interphase. A full lithium-ion battery of 2.3 volts using such an aqueous electrolyte was demonstrated to cycle up to 1000 times, with nearly 100% coulombic efficiency at both low (0.15 C) and high (4.5 C) discharge and charge rates.

ithium-ion (Li-ion) batteries power much of our digital and mobile lifestyle (1, 2). However, their adoption in more strategically important applications such as vehicle electrification and grid storage has been slower, mainly because of concerns raised over their safety, cost and environmental impact (3).

the overall electrochemical stability window of aqueous electrolytes remains constant, anodic stability against oxygen evolution suffers a corresponding compromise, as illustrated by a Pourbaix diagram (9). A maximum voltage of 1.5 V was achieved in aqueous Li-ion batteries, where the residual currents for H_o or O_c evolution still

in water. This leads to an anion-cosolvation sheath, which results in the of a dense interphase on the anode starsing from anion reduction. Combisubstantially reduced electrochemic water at such a high concentration concentrated water-in-salt electrol an expanded electrochemical stabion expanded electrochemical stabion and Mossa, demonstrated an open age (OCV) of 2.3 V and was cycle 100% coulombic efficiency for up to a both low (O.15 C) and high (4.5 at both low (O.15 C) and high (4.5.).

Water-in-salt electrolytes

LiTFSI was chosen as the salt becausolubility in water (>20 m at 25° stability against hydrolysis (15). Whe concentration is above 5 m, the definition applies, as the salt out

solvent in this binary system by both weight and volume (fig. St). In these solutions, the average number of water molecules available to solvate each ion is far below the "solvation numbers" that are well established in conventional electrolytes (-10 m). Instead, interioric attractions become more pronounced relative to solvent-ion interactions, incurring unusual physicochemical properties (fig-20). More important, the inter-

INSIGHTS | PERSPECTIVES

BATTERIES

Opening the window for aqueous electrolytes

Lithium batteries can operate with a safer "water-in-salt" electrolyte

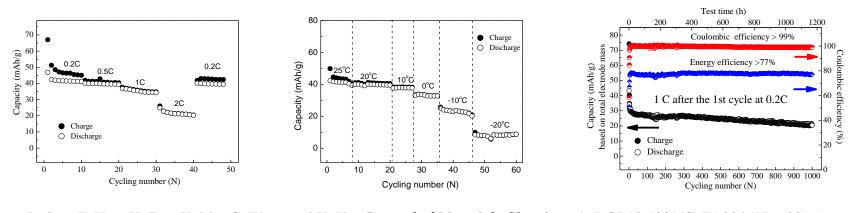
By Leland Smith and Bruce Dunn

y facilitating ion motion between electrodes, electrolytes help to harness the chemical energy in a battery to produce a current and supply usable electric power. Among liquid electrolytes, there are traditional solutions of salt sis can occur. For other electrolyte-electrode combinations, electrolyte breakdown can result in the formation of insoluble solid materials at the electrode surface (4). These decomposition products can widen the effective voltage stability range of the electrolyte above the thermodynamic value.

The electrolyte solvent, salt, and elec-

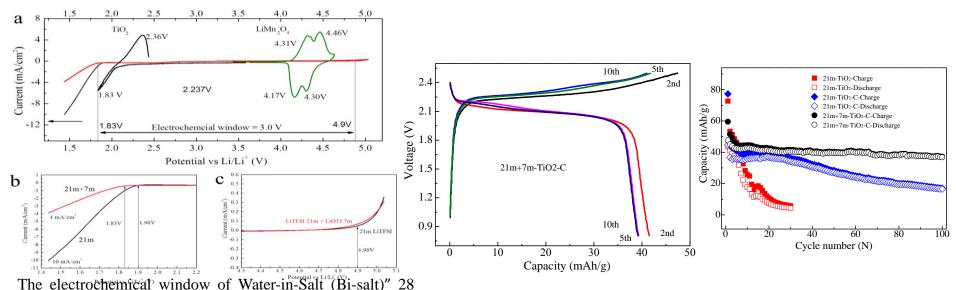
ceeding what is typically obtained from aqueous electrolytes. The high stability is attributed to the electrochemical reduction of bis(trifluoromethane sulforyl)imide at the anode surface, which forms an SEI layer consisting primarily of LiF, and is accompanied by a shift in the oxygen evolution reaction to higher voltages (1).

Long cycle life Aqueous LiFePO₄/Water-in-Salt/Mo₆S₈ Li-ion Battery for Electric Energy Storage



L. Suo, F. Han, X. Fan, H. Liu, C. Wang and K. Xu, Journal of Materials Chemistry A, DOI:10.1039/C6TA00451B, (2016)

High Voltage Li-ion battery using Water-in-Bisalt electrolyte



mLiTFSI-LiTOf electrolyte and the 1st CV traces of active anode (C/TiO₂) and cathode (LiMn₂O₄) materials measured at scanning rate of 0.1 mV/s in the same electrolyte,

Achievement Since the paper in Science

- Further expanded the stability window to 3.1 V
- Employed more energetic electrochemical couple
 - Cathode: LCO, NMC, and LMNO
 - Anode: high capacity anode

Color code:

Red: <100 cycles

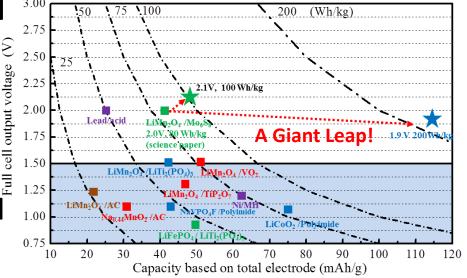
Blue: 100 to 200 cycles

Green: >1000 cycles

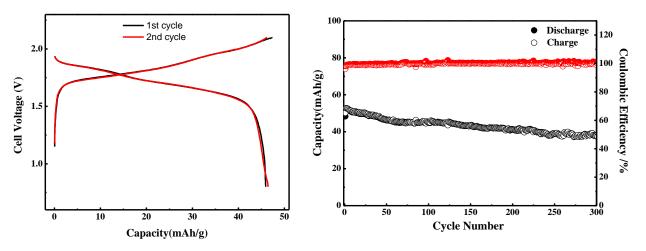
: Our batteries

A Giant Leap: A few aqueous LIB full cells made, energy density up to 200 Wh/(Kg of total electrode mass)

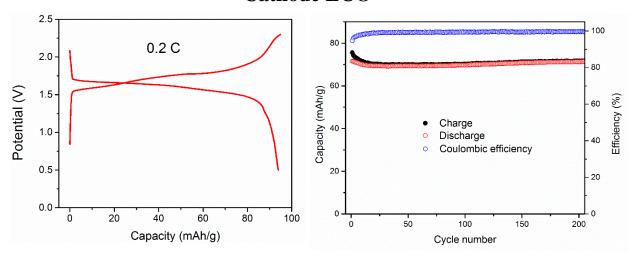
Considering that dry room, BMS, packaging etc could be simplified or eliminated at pack/module level, energy density becomes competitive or even superior to non-aqueous LIB



High Energy Aqueous Li-ion Batteries based on various Chemistries



The cycling of the new 1.9 V aqueous LIB with Mo3S4 and Cathode LCO



The cycling of the new 1.7 V aqueous LIB with Anode Y and Cathode LMO